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ORIGINAL ARTICLE

Catalytic synthesis of 2-(*N*-benzyl-*N*-phenylamino) phenol by mesoporous Pd-doped TiO_2: an environmentally benign approach

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Abstract A facile and environmentally route for catalytic Synthesis of 2-(*N*-benzyl-*N*-phenylamino) phenol under UV irradiation conditions has been developed in the presence of a catalytic amount of mesoporous Pd-doped TiO_2 (Pd/TiO_2) based on a ionic liquid process to fabricate. The particles were characterized with XRD, TEM and XPS. The FT-IR and HNMR spectra confirmed the expected function groups and the structure of 2-(*N*-benzyl-*N*-phenylamino) phenol synthesized.

Keywords Pd-doped TiO_2 · Ionic liquid · 2-(*N*-benzyl-*N*-phenylamino) phenol · Characterization

Introduction

The development of practical methodologies using photo-catalysts which are more environmentally benign is one of the leading concerns of any chemical synthesis (Wang et al. 2009a, b). In recent years, the use of photo-catalysts as an efficient reusable heterogeneous catalyst, to replace traditional method has received considerable attention, due to some advantages such as easy separation, regeneration and reducing corrosion (Zhao et al. 1999; Luo and Sun 2007; Guo et al. 2001; Lermontov et al. 2008; Almeida et al. 2008). *N*-alkylation reaction has been extensively studied owing to their intrinsic properties such as biological activities, electro-chemical responsive and catalytic activities (Abdel-Latif et al. 2007; Gómez-Blanco et al. 2009). However, the classical synthesis involves either the usage of aldehydes and amines. 2-(*N*-benzyl-*N*-phenylamino) phenol as pharmaceutical intermediate is used for synthesis of vasoactive drugs. We have been exploring the catalytic synthetic utility of Pd/TiO_2, and recently found that it could function as a very efficient catalyst for direct synthesis of 2-(*N*-benzyl-*N*-phenylamino) phenol by one-step method with *o*-nitrophenol. Herein, the catalytic behaviors of the photo-catalyst which was prepared by ionic liquids (ILs) with a promising green solvent and the effect of catalysts amounts on catalytic performance were reported.

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Experimental section

Materials

All aqueous solutions were prepared with distilled water. Platinum chloride was obtained from Merck, China. All chemicals were used as received without further purification.

Catalysts preparation

1-Buthyl-3-methylimidazolium hexafluorophosphate [Bmim] $[PF_6]$ was prepared according to the literature (Hao and Zemb 2007; Ding et al. 2007). Nano-structure Pd/TiO_2 catalysts loaded with various palladium amounts on TiO_2 were prepared by ionic liquid method with tetrabutyltitanate as a precursor. For the typical process, Ti $(C_2H_5O)_4$ (5.00 mL) was dissolved into (10.0 mL) [Bmim] $[PF_6]$ under stirring. Subsequently purified water (10.0 mL) which improve the hydrolysis of Ti $(OC_4H_9)_4$ was added to the above solution under stirring. After 4 h, precipitates were produced which were gathered by filtration,

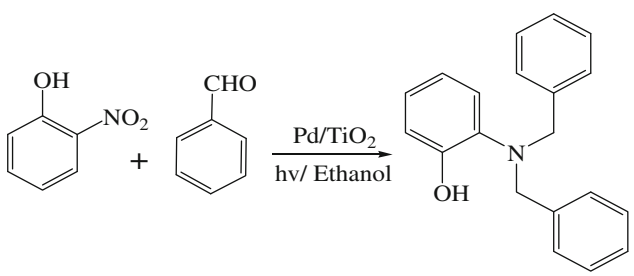
thoroughly washed with distilled water, then dried at 80 °C for 3 h, and finally the white powders were obtained. The powders were added into the 1.2 g palladium chloride solution under stirring for 3 h, the mixture was dried in an oven at 80 °C for 8 h, calcined in a furnace at 350 °C for 2 h. The prepared catalysts were characterized by N_2 adsorption–desorption, XRD and FESEM.

Catalytic synthesis of 2-(*N*-benzyl-*N*-phenylamino) phenol

Catalytic reactions using o-nitrophenol (ONP) and benzaldehyde as materials were performed at atmospheric pressure and room temperature in a glass reactor (Scheme 1). The suspending solution, which was composed of an ratio (1:2.1) of o-nitrophenol (720 mg) and benzaldehyde and 500 mg of Pd/TiO_2 along with 50 mL of ethanol solvent in the photoreactor was irradiated using a 500 W high-pressure mercury lamp (356 nm) under magnetic stirring at room temperature. After irradiation for 30 min the reaction mixture was centrifuged to separate the catalyst and the pure products were isolated by recrystallization for three times. Product conversion was analyzed by HPLC chromatography. Further analysis was performed by FT-IR, LCMS and ^1H NMR spectra measurement.

The characterization apparatus

The catalytic crystal phase was determined from the X-ray diffraction (XRD) patterns obtained by an X-ray diffractometer (Model D/Max 2550 V) using Cu Kα radiation (1.54178 Å), performed over angular ranges of $2\theta = 20–70°$. The surface property of Pd/TiO_2 sample was characterized by X-ray photoelectron spectroscopy (XPS) in a VG ESCALAB250 system with a monochromatic Al Kα radiation (225 W, 15 mA, 15 kV, vacuum degree 7×10^{-10} mbar) and binding energies were calibrated using C1 s hydrocarbon peak at 284.6 eV. N_2 adsorption–desorption isotherms were obtained at 77 K using an accelerated surface area and porosimetry system 2,020 m apparatus (Micromeritics). The synthesis products were analyzed (4,000–500 cm^{-1}) on the Fourier transform infrared spectroscopy (FT-IR) applying the KBr disc technique and HNMR spectra (300 MHz, DMSO, ppm).



Scheme 1 Synthesis of 2-(*N*-benzyl-*N*-phenylamino) phenol with nanoparticle Pd/TiO_2 under UV irradiation

Results and discussion

N_2 adsorption–desorption analysis

As shown in Fig. 1, the FETEM (JSM-6700F, samples covered by thin gold-film) morphologies revealed that TiO_2 sample was present in the irregular nanoparticles from 50 to 100 nm, but the nanoparticles in Pd/TiO_2 are distributed in the nanoparticles more homogeneously with similar particle size around 5–20 nm. Addition of platinum chloride does not significantly affect the particle morphology, except for a slight decrease in the level of particle aggregation and an associated increase in interparticle voids. So modification with platinum chloride further improved the particle distribution and the layer-by-layer shape.

N_2 adsorption–desorption analysis

The porosity of the catalysts was studied by measuring gas N_2 adsorption at 77 K. Shown in Fig. 2, a type-IV isotherm is showed in N_2 adsorption–desorption curve. The possible formation mechanism of porous structure Pd/TiO_2 particles is that the special structure of ILs which implies that it successfully participates in the reaction as a self-assembling template (Zhou and Antonietti 2003). It is believed the combination of ionic liquid-template effects with so-called reaction limited aggregation resulted in the porous Pd/TiO_2 (Hu et al. 2008).The pore size distributions have been determined by referring to the BJH model applied to desorption isotherm branch. The porous diameter is centered at 34 nm and the surface area is more than 112 m^2/g. The effective for aggregation of the Pd/TiO_2 particles without accompanying any shrinkage and collapse of the net structure in the presence of ILs is due to the low interface energy of ILs which makes the velocity of initial Pd/TiO_2 nuclei growth better than in water.

XPS and XRD analysis

The TiO_2-supported Pd catalyst was characterized using X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRD). The XPS results (Fig. 3) show that the surfaces of the metal nanoparticles in the calcined catalyst material are significantly enriched with Pd. It could be seen from Fig. 3 that the Pd3d peak was found at 339.5 eV, which was attributable to Pd anions resulting from substitution for oxygen sites by pd atoms in the TiO_2 though its intensity was very weak (Enache et al. 2006). It has been

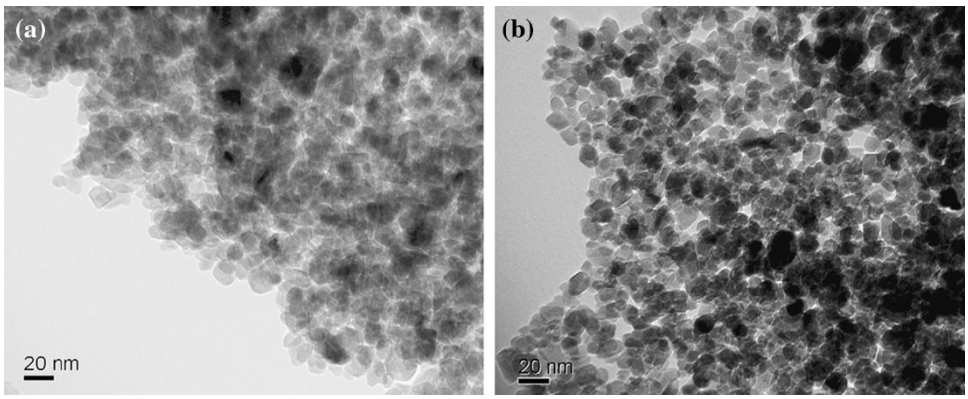


Fig. 1 FETEM images of TiO_2 (**a**) and Pd/TiO_2 (**b**) catalysts prepared

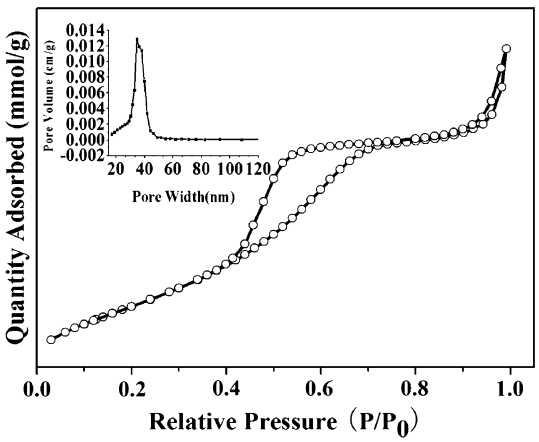


Fig. 2 The N_2 adsorption–desorption curve and BJH pore-size distribution (*inset*) of Pd/TiO_2 catalyst

analyzed that the peak appeared around 341 eV was attributed to the Pd atoms from Pd–Pd, Pd–H, O–Pd, or Pd-containing organic compounds adsorbed on the surface, and the signal a was Pd bound to O, C, or Pd atoms, so it was concluded the Ti–O–Pd bonds could had been formed. The crystalline phase of Pd/TiO_2 was analyzed by X-ray diffraction. Figure 4 shows the XRD patterns of Pd/TiO_2. It indicates other crystal phase can be detected. The strongest peak at $2\theta = 25.3°$ is representative of (101) anatase phase reflections. The peaks position of Pd/TiO_2 had not shifted, which indicated that Pd/TiO_2sample did not exhibit additional phases except anatase. Furthermore, the average crystalline size of Pd/TiO_2 calculated using the Scherrer's formula was about 8 nm. As seen in TEM photos presented, the particle size after modified by platinum chloride change. And this is in agreement with the XRD study. Because the little particles can cause the aggregation of TiO_2 nanoparticles and when the particles are modified by platinum chloride, the Pd atom was substitutionally doped into the TiO_2 lattice. We think that Pd surface segregation occurs during calcination to produce alloy nanoparticles forming the Pd–Ti or Pd–O–Ti surrounding TiO_2. So the particles are uneasy to produce the aggregation and the particle size changes.

Catalytic synthesis of 2-(*N*-benzyl-*N*-phenylamino) phenol

The HPLC yields to synthesis of 2-(*N*-benzyl-*N*-phenylamino) phenol by pure TiO_2 and Pd/TiO_2 have also been obtained. The results are shown in Table 1. Obviously, the reaction was not carried out without the catalyst and photoirradiation. And the yield is only 0.6 % by use of pure TiO_2. The yield of 2-(*N*-benzyl-*N*-phenylamino) phenol increases with the rise of catalyst amount, obtaining yield to 2-(*N*-benzyl-*N*-phenyl-amino) phenol higher than 85 %. This fact can be explained taking into account the photocatalytic activity of Pd/TiO_2 calcined at 350 °C catalyst for reduction of nitro compounds. Higher catalyst concentration brings about an increase in the photogenerated electron in the surface of catalyst, resulting into an improvement of reducing activity. However, when the amount was attained to 10.0 wt%, the yield hardly increased. Maybe the active sites are covered by Pd/TiO_2 and the path-length of

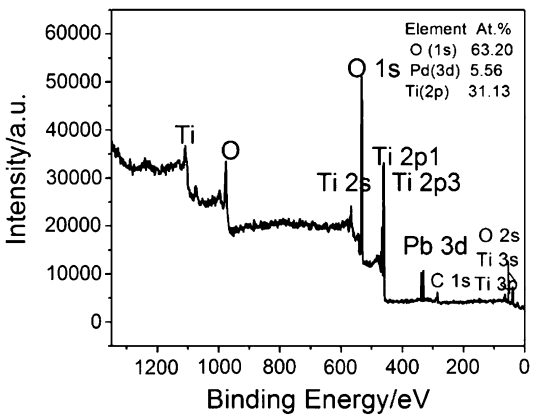


Fig. 3 XPS spectra of Pd/TiO_2 prepared by the ionic liquid method

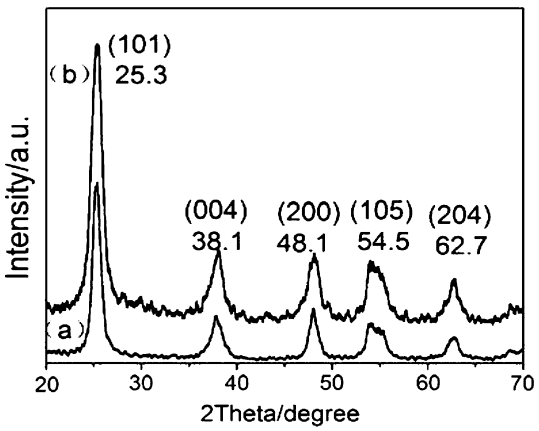


Fig. 4 XRD patterns of *a* TiO_2 and *b* Pd/TiO_2

Table 1 Effect of catalysts amount on catalytic performances of catalysts prepared for synthesis

Entry	Catalyst	Amounts (wt %)	Photoirradiation time (min)	Yield (%)*
1	P25	1.0	30	0
2	TiO_2	1.0	30	0.6
3	Pd/TiO_2	0	30	0
4	Pd/TiO_2	1.0	0	0
5	Pd/TiO_2	1.0	30	76.3
6	Pd/TiO_2	4.0	30	87.4
7	Pd/TiO_2	8.0	30	89.5
8	Pd/TiO_2	10.0	30	86.7

* HPLC yield. Synthetic conditions: $T = 303$ K; ONP/benzaldehyde = 1/2.1; reaction time, 30 min

photons entering the solution decreases. Consequently, the number of electron attacking the compound formed on the surface of Pd/TiO_2 involves to the reduction efficiency. However, the doped nanoparticles show the highest photocatalytic activity. This not only depended on the small particle size, but it may also result from the Pd dopant sites, which may be the most important (Ohtani et al. 1986; Wang et al. 2009a, b).

Further analysis was performed by isolated the products whose isolated yield is 72.4 %. FTIR spectra of the synthesized compounds showed the following absorption bands at 1,632 cm^{-1} (ν_{C-N}), ~3,450 cm^{-1} (ν_{-OH}), 1,585, 1,456 cm^{-1} (ν_{C-C}), and ~1,230 cm^{-1} (ν_{C-O}). The absorption peaks at 2,820–2,720 cm^{-1} is the characteristic values of ν_{C-H}. But there were no peaks about aldehyde and ONP according to the spectra. It indicated that benzaldehyde and ONP did not exist in the produces. The FT-IR spectra confirmed the expected function groups in the *N*-alkylation synthesized reaction. LCMS: (ES, m/z): $[M + H]^+$ 290. HNMR: (300 MHz, DMSO, ppm) δ: 7.586 (1H, s), 7.754 (1H, s), 7.806 (1H, s), 7.460 (1H, s), 7.272–7.14 (10H, s), 5.521 (1H, s), 4.67 (4H, s).

Conclusions

Photocatalyst Pd/TiO_2 synthesized with ionic liquid: [Bmim] PF_6 as reaction medium have been considered as an efficient catalyst for the synthesis of 2-(*N*-benzyl-*N*-phenylamino) phenol. The catalyst prepared exhibits significantly high activity and the pores and anatase phase of Pd/TiO_2 nanoparticles have been investigated.

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